

Analysis of Molecular Rotational Spectra

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Abstract

Rotational spectra of diatomic molecules measured in the high-precision experiments are analyzed. Such a spectrum is usually fitted by an 8th order polynomial in spin. In fact, from the theoretical point of view, the rotational spectrum is expected to be a smooth function of spin. Thus, fitting the rotational spectrum in terms of a low order polynomial in spin seems to be justified. However, this is not what we found in the present work. We show that the measured spectrum is not necessarily a smooth function of the spin, which is quite surprising. Whether or not it indicates the presence of some hidden physics is an open question.

I. INTRODUCTION

Characteristic quantities of a diatomic molecule are the energy associated with the motion of electrons and the one associated with the motion of two nuclei (ionic cores). The latter motion is essentially that of a dumbbell shaped system (vibration against one another and rotation as a whole). The order of magnitude of the electronic vs. vibrational excitation energy (E_{ele}/E_{vib}) is typically 100 and that of the vibrational vs. rotational one (E_{vib}/E_{rot}) another 100. It means that E_{vib} (E_{rot}) corresponds to transitions in the near (far) infrared. Thus, the electronic motion is very fast compared with that of nuclei, so that its wavefunction may be constructed from the instantaneous constellation of two nuclei assuming as if nuclei were frozen and thus depends parametrically on the positions of two nuclei (Born-Oppenheimer approximation). This is the standard way of decoupling the electronic and nuclear degrees of freedom from one another. The treatment of the nuclear part then becomes very simple.

The nuclear radial Schrödinger equation (with $\hbar = 1$) takes the form

$$\frac{1}{2M} \frac{d^2 \psi_{VI}(r)}{dr^2} + \left[E_V(I) - U(r) - \frac{I(I+1)}{2Mr^2} \right] \psi_{VI}(r) = 0 \quad (1)$$

where r is the distance between two nuclei and M the reduced mass. The potential $U(r)$ between two nuclei is a complicated object that involves an integration over the electronic wavefunction, which we do not go into here. In practice, it is phenomenologically replaced by a Morse potential. The quantum number I is the rotational spin which characterizes the angular wavefunction $Y_{IM}(\theta, \phi)$ and V the so-called vibrational quantum number which characterizes the radial wavefunction. We note that, because of the mathematical property of this equation, *the eigenvalue $E_V(I)$ has to be an analytic function of the parameter (spin) I* . Since the effective potential

$$V(r) = U(r) + \frac{I(I+1)}{2Mr^2} \quad (2)$$

has a prominent minimum at $r = r_0$, where r_0 is of the order of the molecular size, one usually expands it around $r = r_0$ ($\left[\frac{dV(r)}{dr} \right]_{r=r_0} = 0$) and expresses $V(r)$ in a power series of

$r - r_0$. Consequently, the radial motion can be treated as a vibration having a perturbing unharmonicity. The dependence of $E_V(I)$ on I becomes then a power series of $I(I + 1)$ and one usually stops the series at the 8th order in I :

$$E_V(I) = T_V + B_V I(I + 1) - D_V [I(I + 1)]^2 + H_V [I(I + 1)]^3 + L_V [I(I + 1)]^4 \quad (3)$$

In recent years, very accurate data of rotational spectra in diatomic molecular bands became available thanks to modern experimental techniques [1–8]. What is measured in such an experiment is the so-called R- and P-process [9]

$$R(I) = E_H(I + 1) - E_L(I), \quad P(I) = E_H(I - 1) - E_L(I). \quad (4)$$

These quantities are the ‘inter-band’ $\Delta I = 1$ (dipole) transition energies between a higher ($V = H$) and a lower ($V = L$) vibrational band and are usually measured in the unit of wave number (cm^{-1}). The coefficients in the formula (3) have been fitted to such experimental data [1–8]. However, one can take a different approach [10].

By inverting the relation (4), one obtains the ‘intra-band’ $\Delta I = 2$ (quadrupole) transition energy $\Delta E_V(I) \equiv E_V(I) - E_V(I - 2)$ as

$$\Delta E_H(I) = R(I - 1) - P(I - 1), \quad \Delta E_L(I) = R(I - 2) - P(I) \quad (5)$$

for the higher and lower band, respectively. It should be remarked that, from the set of data of R- and P-process, one obtains four separate sets of data $\Delta E_V(I)$ for $V = H$ and $V = L$ bands with even as well as odd spin sequences. The intra-band transition energy should be a smooth function of spin I according to the theoretical consideration made in the beginning. In the present work, we want to examine this statement. We will in fact show that the measured intra-band transition energies are not necessarily smooth functions of spin. Let us first devise a tool which suits the analysis of data.

II. THE METHOD OF ANALYSIS

To study the behavior of $\Delta I = 2$ transition energy $\Delta E(I) = E(I) - E(I - 2)$ for each band ($V = H$ or L) and each spin sequence ($I = \text{even}$ or odd), some kind of data

manipulation is necessary. In fact, if one plots the quantity $\Delta E(I)$ directly, it is hardly possible to see any fine structure since $\Delta E(I)$ is a globally increasing function of I and extends over a wide range of values. Thus, the basic idea is to look at the deviation of the transition energy $\Delta E(I)$ from its smoothly increasing part.

To this purpose, we subtract a polynomial of order N in I from $\Delta E(I)$ and define what we call the N th order one-point formula [11]

$$\Delta_N^{(1)} E(I) \equiv \Delta E(I) - Q_N(I), \quad Q_N(I) = \sum_{m=0}^N q_m I^m \quad (6)$$

where the coefficients q_m are determined by minimizing the quantity

$$\chi(q_0, \dots, q_N) \equiv \left[\Delta_N^{(1)} E(I) \right]^2 \quad (7)$$

with respect to q_m ($\frac{\partial \chi}{\partial q_m} = 0$). This leads to a set of $N + 1$ equations ($m = 0, 1, \dots, N$)

$$\sum_{n=0}^N S_{mn} q_n = T_m, \quad S_{mn} \equiv \sum_I^{\Delta I=2} I^m I^n, \quad T_m \equiv \sum_I^{\Delta I=2} I^m \Delta E(I). \quad (8)$$

We note that the smooth part $Q_N(I)$ which we subtract from $\Delta E(I)$ is nothing other than a polynomial of order N determined by the χ -square fit to $\Delta E(I)$. However, in practice, this formula cannot be used in the present form particularly when the order of the polynomial N is larger than 3 since the equation (8) is highly ill-conditioned. Thus, in what follows, we want to transform it into another form.

First, let us note that the replacement $I \rightarrow I - I_0$ does not change the fitting procedure since the shape of the polynomial $Q_N(I)$ as a function of I is unchanged. Thus, the origin of the spin values can be shifted freely. Secondly, the spin variable can be scaled too ($I \rightarrow aI$) since the order of the polynomial remains the same. These properties can be used to rewrite the polynomial in a different form.

Shifting and scaling the spin values can be achieved most generally by a linear mapping $I = ax + b$. The increment of x is thus $\Delta x = \frac{\Delta I}{a}$ ($\Delta I = 2$). We will choose $a = \frac{I_{max} - I_{min}}{2}$ and $b = \frac{I_{max} + I_{min}}{2}$ so that the range of x becomes $[-1, +1]$, where $x = -1$ ($+1$) corresponds to $I = I_{min}$ (I_{max}). The polynomial in question may thus be written in the form

$$Q_N(I) = \sum_{m=0}^N p_m P_m(x). \quad (9)$$

Here, we use the Legendre polynomial $P_m(x)$ instead of x^m . The reason will be explained below. The resulting set of equations is similar to (8) but q_n is replaced by p_n and I^n (I^m) by $P_n(x)$ ($P_m(x)$). This representation has an advantage that there holds the relation

$$S_{mn} = \sum_{x=-1}^{+1} P_m(x)P_n(x) = 0 \quad \text{if } m+n = \text{odd}. \quad (10)$$

It means that the whole set of equations splits into two independent sets of equations of smaller dimensions, one with $m, n = \text{even}$ and the other with $m, n = \text{odd}$:

$$\sum_{n=\text{even or odd}}^N S_{mn}p_n = T_m, \quad S_{mn} \equiv \sum_{x=-1}^{+1} P_m(x)P_n(x), \quad T_m \equiv \sum_{x=-1}^{+1} P_m(x)\Delta E(I). \quad (11)$$

This set of equations determines the coefficients p_m and accordingly the polynomial (9) which represents the smooth part of $\Delta E(I)$.

It remains to be remarked that the original set of equations (8) is highly ill-conditioned. It is indeed so ill-conditioned that even the double precision algorithm is not free from the numerical instability caused by large losses of accuracy if N is greater than 3. This problem can be avoided by shifting and scaling the spin values as presented above. In fact, the situation improves slightly if one uses the power series x^m thanks to a property analogous to (10). Nevertheless, this does not fully resolve the numerical instability. The reason lies basically in the fact that the zeros of x^m are multiple and are all concentrated at $x = 0$. In contrast, all zeros of $P_m(x)$ are simple and never coincide with one another for different m 's. The use of the Legendre polynomial $P_m(x)$ instead of the power series x^m is thus essential for the numerical reliability (both accuracy and stability). A similar caution may be necessary when fitting the formula (3) to experimental data.

In the next section, we will present $\Delta_N^{(1)}E(I)$ for a number of experimental data using a 7th order polynomial. In fact, $N = 7$ is quite appropriate for the analysis of molecular rotational spectra since the rotational spectrum for a given vibrational band is fitted (globally) by a formula containing up to the 8th order in spin I (see eq.(3)) so that the transition energy $\Delta E(I)$ is a 7th order polynomial.

We will also define the ‘filtered’ one-point formula by setting the quantity $\Delta_N^{(1)}E(I)$ to zero if its absolute value is smaller than or equal to the corresponding error bar. This

formula is quite useful in practice. By construction, it shows whether the deviation of the transition energy $\Delta E(I)$ from its smooth part is physically significant or not.

III. ANALYSIS OF EXPERIMENTAL DATA

As mentioned before, we obtain four sets of transition energies $\Delta E(I)$ (even and odd spin sequence for higher and lower band) from the measurement of $R(I)$ and $P(I)$. Thus, four independent sets of data $\Delta_N^{(1)} E(I)$ can be created, which we present as diagrams.

As an example, we plot in Fig.1a the 7th order one-point formula $\Delta_7^{(1)} E(I)$ obtained from the measured $R(I)$ and $P(I)$ of the 2-2 band of the $A^1\Sigma^+ - X^1\Sigma^+$ system of the molecule YN [4]. On the other hand, Fig.1b shows the corresponding filtered one-point formula. It is ‘filtered’ in the sense that we take

$$\Delta_N^{(1)} E(I) = 0 \quad \text{if} \quad |\Delta_N^{(1)} E(I)| \leq \text{Error Bar} \quad (12)$$

where Error Bar is twice the error bar of the measurement of $R(I)$ and $P(I)$, see eq.(5). Eq.(12) makes easily visible that some deviations of the transition energy from the smooth part that occur in Fig.1a are physically insignificant as they are zero within the Error Bar. Thus, if the rotational spectrum is indeed a smooth function of spin I , which is what we want to confirm, the deviation should be zero everywhere when filtered. However, Fig.1b clearly shows that there remain some deviations which are not filtered away to zero ($V = H$ band). These deviations are beyond the Error Bar and may thus be considered as significant. This is rather surprising but is not a single case. We found many such cases, most of them being more complicated than this example. It should be emphasized that the filtered formula clearly shows at which spins the anomaly occurs.

We present another example. Figs.2a and 2b show respectively the one-point formula and the corresponding filtered formula applied to the 1-1 band of the $C^1\Sigma^+ - X^1\Sigma^+$ system of the molecule YD [5]. One sees a behavior similar to the above example, though it looks slightly complex. As a matter of fact, this kind of results is seen also in the 0-0 and 1-0 bands of the $A^6\Sigma^+ - X^6\Sigma^+$ system of the CrD molecule [6]. Actually, there are

many more complex cases in the data we have analyzed, some of which will be shown later. Thus, it seems that there exists anomaly (irregularity) in the measured spectrum and the question is where it comes from.

We have examined the relation between a spectrum and the resulting irregularity which appears in the transition energy. Suppose that there is a band crossing in a spectrum. It will produce a kink at the crossing point and thus an irregularity in the transition energy. While it is unlikely that a band crossing may occur in the molecular cases, it indeed exists in the nuclear cases [11], which leads to the so-called backbending phenomenon. Based on this observation, we have studied a model in which a smooth rotational spectrum $E(I) = AI(I + 1)$ has a sequence of kinks around a spin $I = I_0$. Since the smooth part of the transition energy $\Delta E(I) = E(I) - E(I - 2) = 2A(2I - 1)$ is a first order polynomial in I , it will be sufficient to use the 1st order one-point formula $\Delta_1^{(1)}E(I)$ in such a demonstrative example. Some of them are presented in Fig.3.

The three-kink model in Fig.3 is of particular interest to the YN molecule [4] as it reproduces the $V = H$ even spin data shown in Fig.1b while the $V = H$ odd spin data corresponds to a special four-kink model. The three-kink spectrum in Fig.3 was produced by shifting ‘down’ the energy from a smooth curve $E(I) = AI(I + 1)$ at a spin $I = I_0$ while the pattern with exactly opposite phase will be obtained by shifting ‘up’ the energy. In general, a spectrum with a given number of kinks can produce several different patterns depending on the way how the kinks are created.

Let us next examine the YD molecule [5] presented in Fig.2b. The $V = H$ even spin data can also be understood in terms of a three-kink model, in which three-fold kinks occur at two different places (at $I = 18$ and 32 in a spectrum of the form $E(I) = AI(I + 1) - B[I(I + 1)]^2$). Fig.4 compares the data and such a ‘theory’. The experiment is reproduced quite well. On the other hand, the $V = H$ odd spin data seems to suggest the presence of different types of kinks that occur at three different places. In fact, the first one (at the lowest spin region) shows obviously a two-kink pattern while the last one (at the highest spin region) a four-kink pattern, cf. Fig.3. Finally, the middle one is more complicated but one can easily guess that it is a six-kink pattern.

Therefore, whatever the reason may be, it is certain that there exist various types of kinks that occur locally at different places in these rotational spectra. In other words, *they are for sure not smooth (or analytic) functions of the spin.*

IV. CONCLUSION

We have shown that the molecular rotational spectrum is not necessarily a smooth function of spin according to the measurements of $R(I)$ and $P(I)$ as well as the error estimate of the measurements. This is quite surprising because of our theoretical understanding that the spectrum has to be an analytic function of spin I , which follows from the equation (1) obtained by assuming the Born-Oppenheimer approximation. Since it is rather difficult to believe that this approximation is violated, the first thought occurred to us was that there should be some error in the input file to our Fortran code because even a single error in typing data would create ‘artificial’ kinks. It may also be worth reconfirming all data at different laboratories with different experimental setups.

In the previous section, we have shown relatively simple examples but there are actually many more complex cases. Fig.5 shows the filtered one-point formula applied to the 0-0 band belonging to the $B^1\Sigma_u^+ - X^1\Sigma_g^+$ system of the $^{63}\text{Cu}_2$ molecule [2]. Nevertheless, it is likely that this result can also be decomposed and classified into various patterns as we have done in the previous section. We believe that this way of understanding the experimental data is suggestive and that intensive (phenomenological) studies along this line will give a useful clue. The aim of the present work is to initiate such a study¹. One day, we may then be able to find the real physical implication lying behind this ‘new’ phenomenon, although whether or not it contains something new is an open question.

¹The Fortran source code used in the present work may be distributed upon request. Send an email to khara@physik.tu-muenchen.de or glalazis@physik.tu-muenchen.de.

REFERENCES

- [1] D. E. Mann, B. A. Thrush, D. R. Lide Jr., J. J. Ball and N. Acquista, J. Chem. Phys. **34** (1961) 420
- [2] R. S. Ram, C. N. Jarman and P. F. Bernath, J. Mol. Spectrosc. **156** (1992) 468
- [3] R. S. Ram, C. N. Jarman and P. F. Bernath, J. Mol. Spectrosc. **161** (1993) 445
- [4] R. S. Ram and P. F. Bernath, J. Mol. Spectrosc. **165** (1994) 97
- [5] R. S. Ram and P. F. Bernath, J. Mol. Spectrosc. **171** (1995) 169
- [6] R. S. Ram and P. F. Bernath, J. Mol. Spectrosc. **172** (1995) 91
- [7] G. Tai and R. D. Verma, J. Mol. Spectrosc. **173** (1995) 1
- [8] R. S. Ram, P. F. Bernath and S. P. Davis, J. Mol. Spectrosc. **173** (1995) 146
- [9] G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules*, van Nostrand, 1963
- [10] D. Bonatsos, C. Daskaloyannis, S. B. Drenska, G. A. Lalazissis, N. Minkov, P. P. Raychev and R. P. Roussev, Phys. Rev. **A54** (1996) R2533
- [11] K. Hara and G. A. Lalazissis, Phys. Rev. **C55** (1997) 1789

FIGURE CAPTIONS

Fig. 1 (a) Seventh order one-point formula and (b) the corresponding filtered formula applied to the YN data [4]

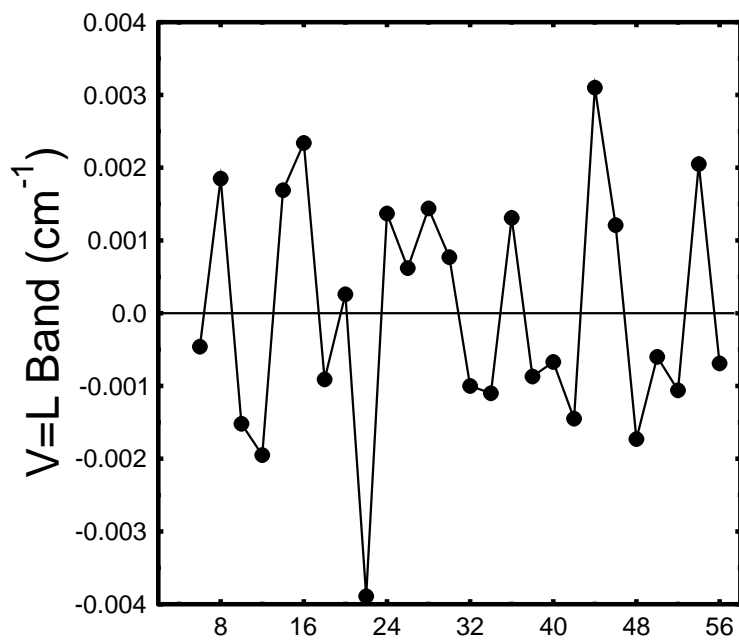
Fig. 2 (a) Seventh order one-point formula and (b) the corresponding filtered formula applied to the YD data [5]

Fig. 3 Model spectra that have two, three and four successive kinks and the irregularities that occur in the one-point formula

Fig. 4 Comparison between the $V = H$ even spin data of the YD molecule (cf. Fig. 2b) and a three-kink ‘theory’

Fig. 5 Seventh order filtered one-point formula applied to the $^{63}\text{Cu}_2$ data [2]

Even Spin



Odd Spin

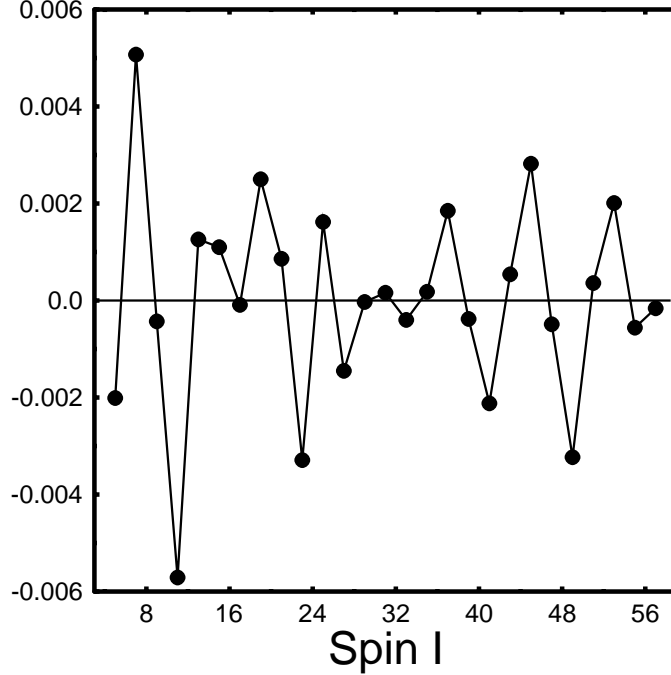
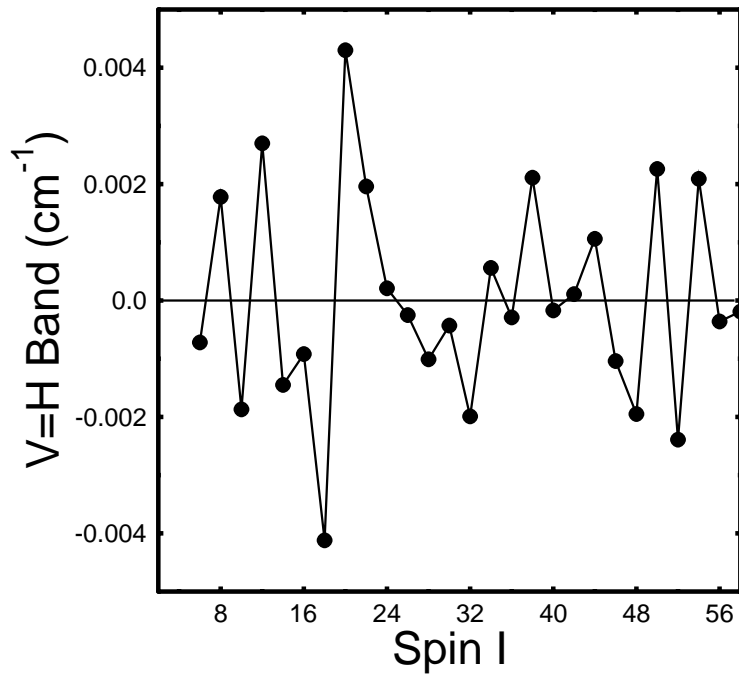
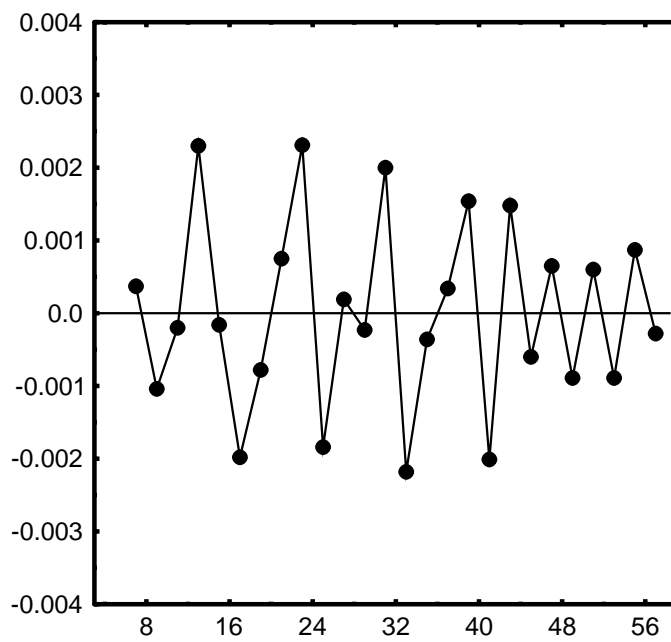
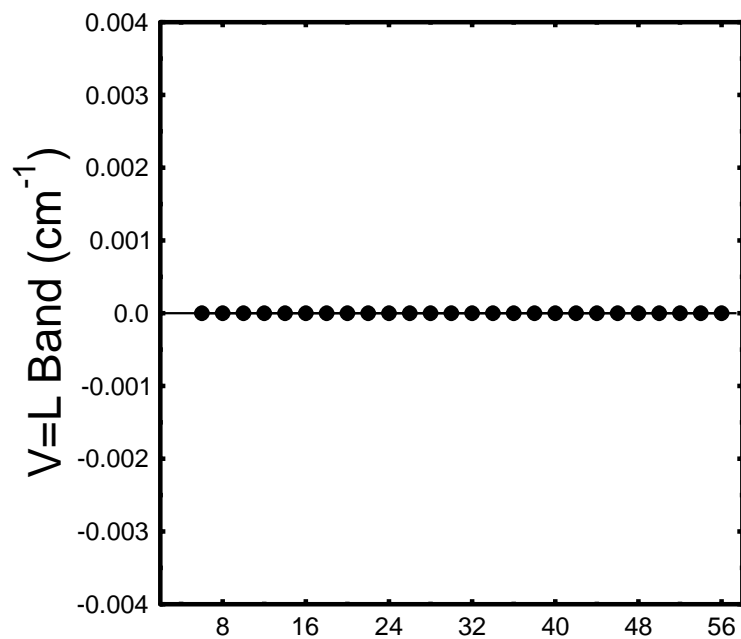


Fig. 1a

Even Spin



Odd Spin

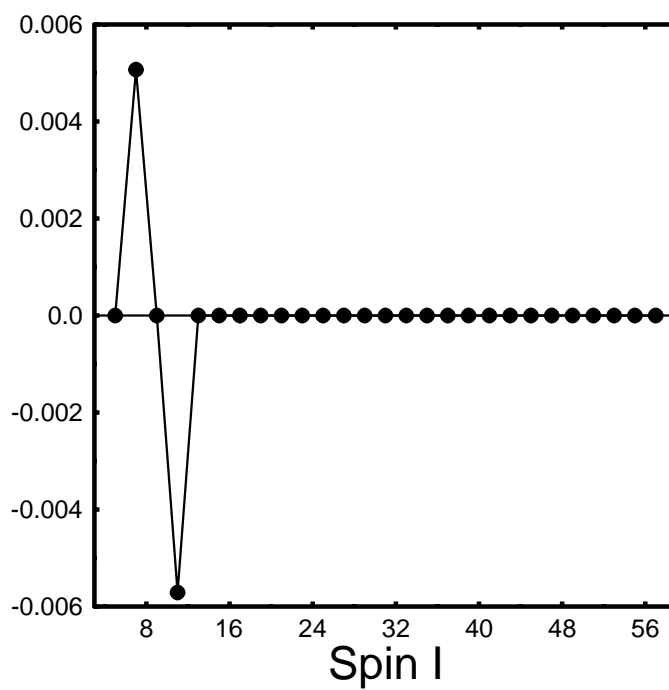
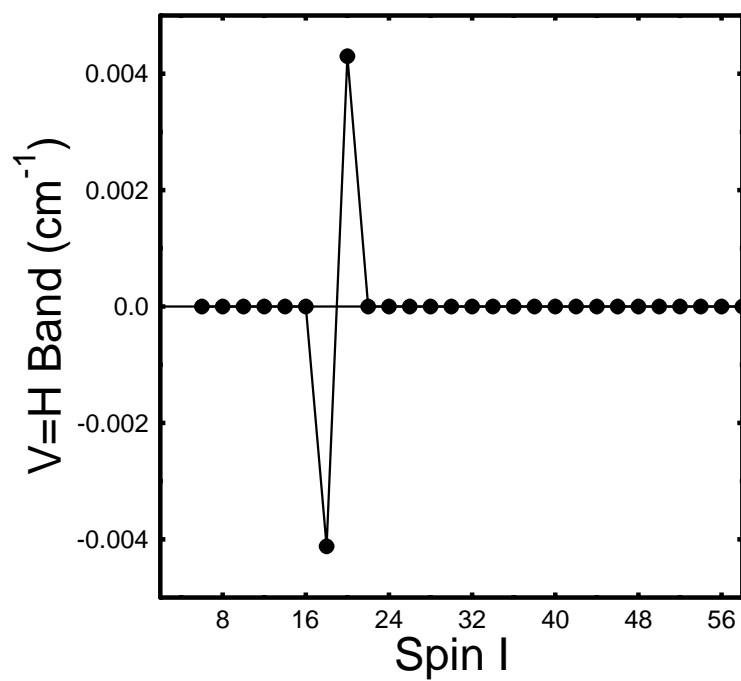
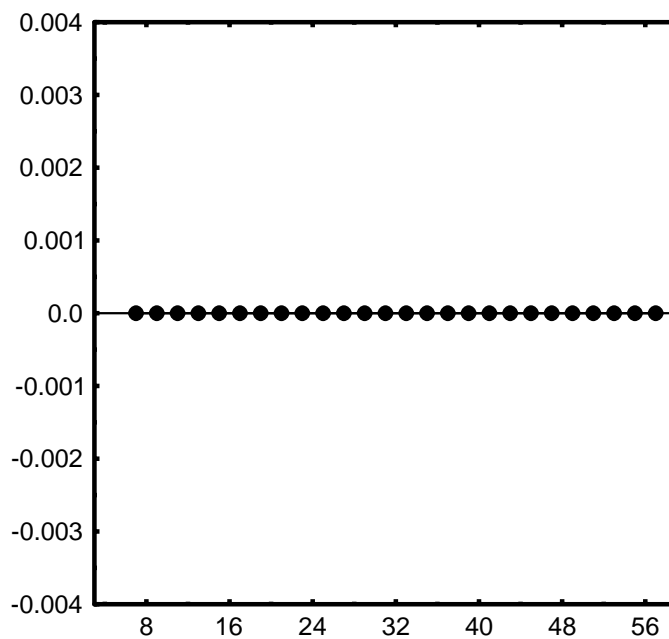
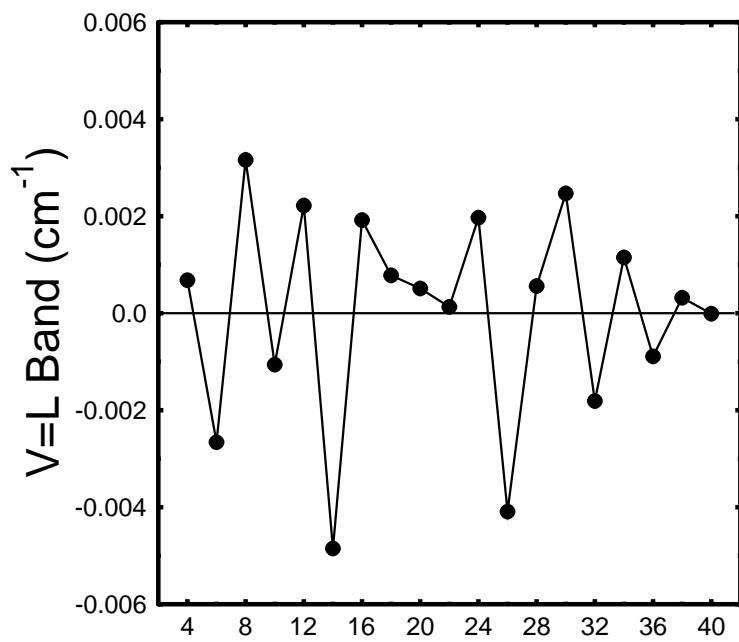


Fig. 1b

Even Spin



Odd Spin

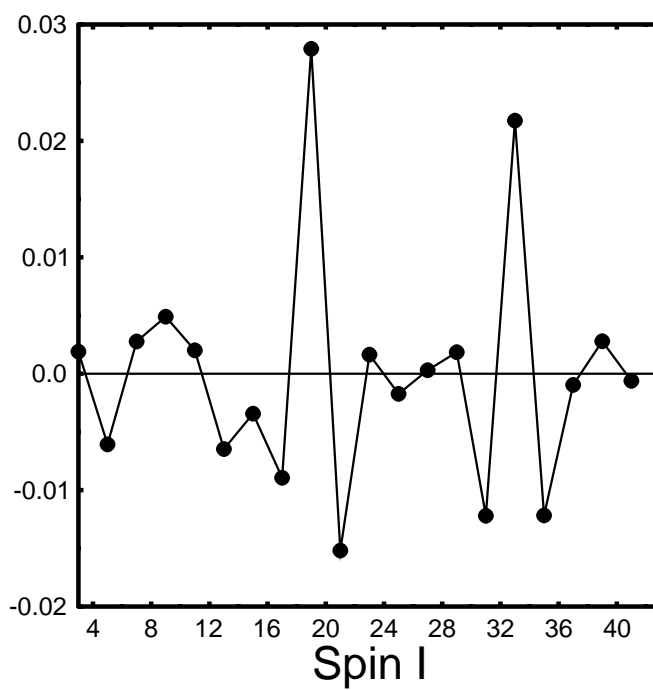
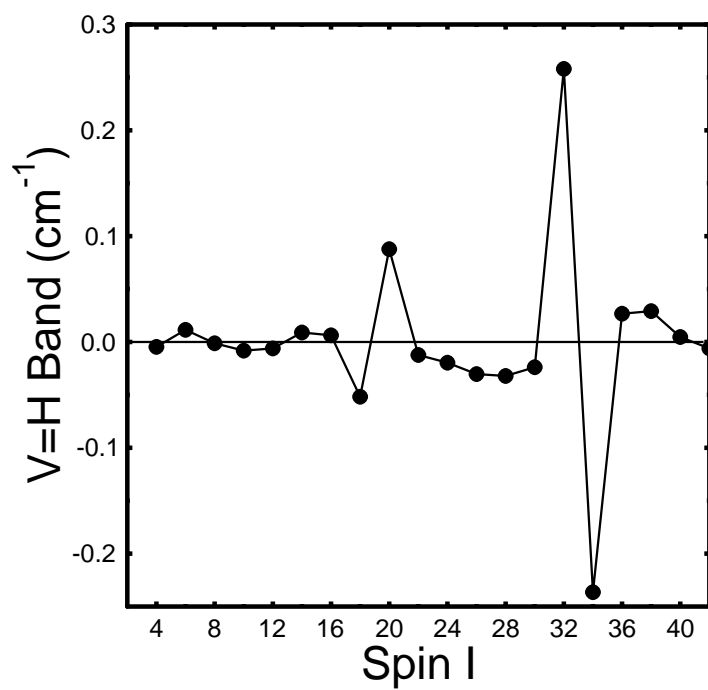
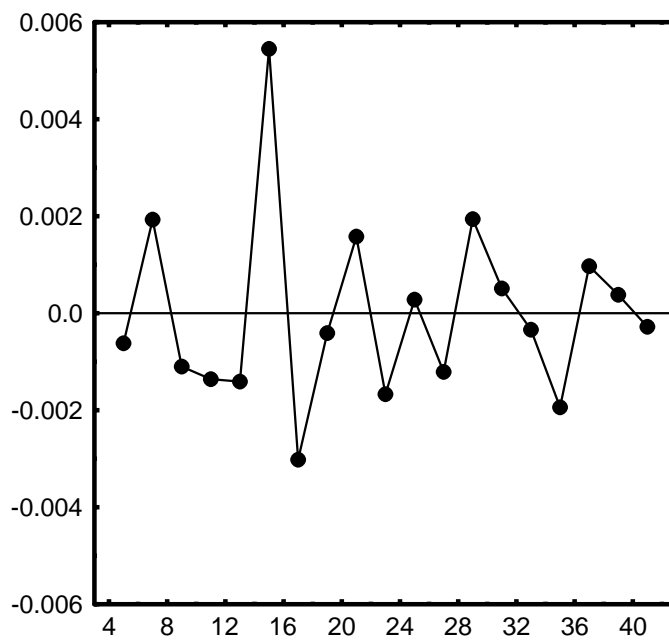
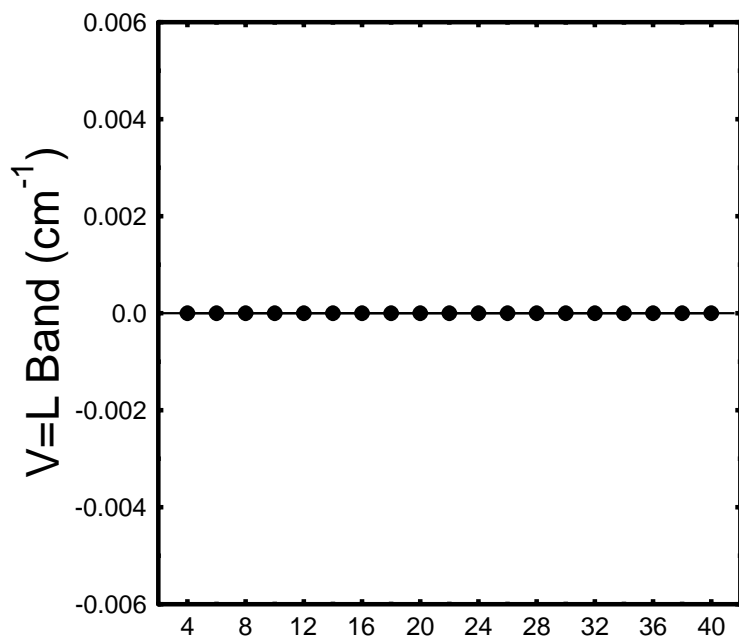


Fig. 2a

Even Spin



Odd Spin

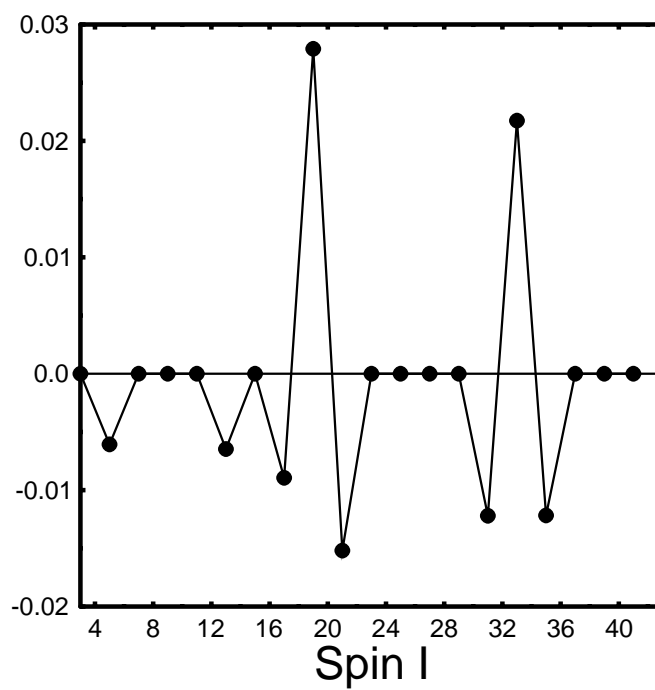
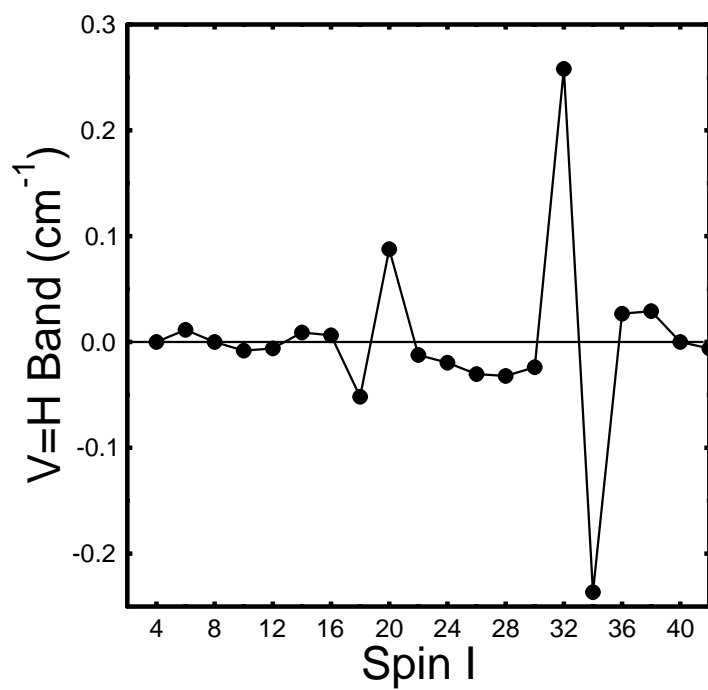
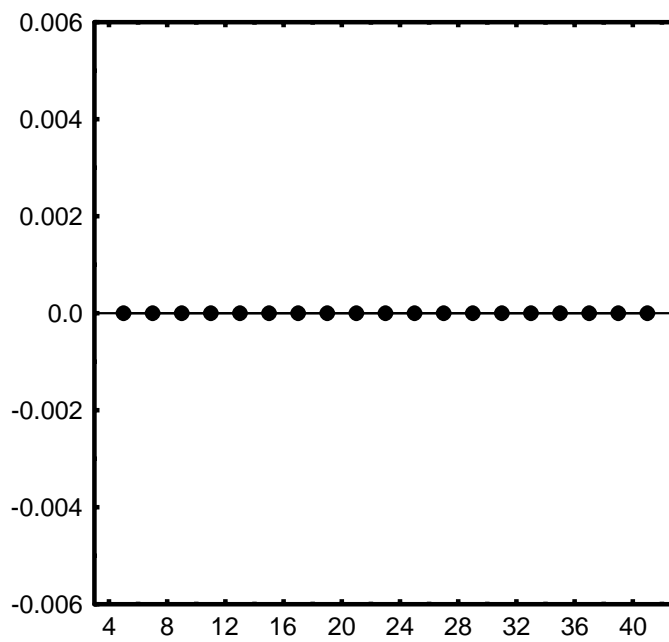


Fig. 2b

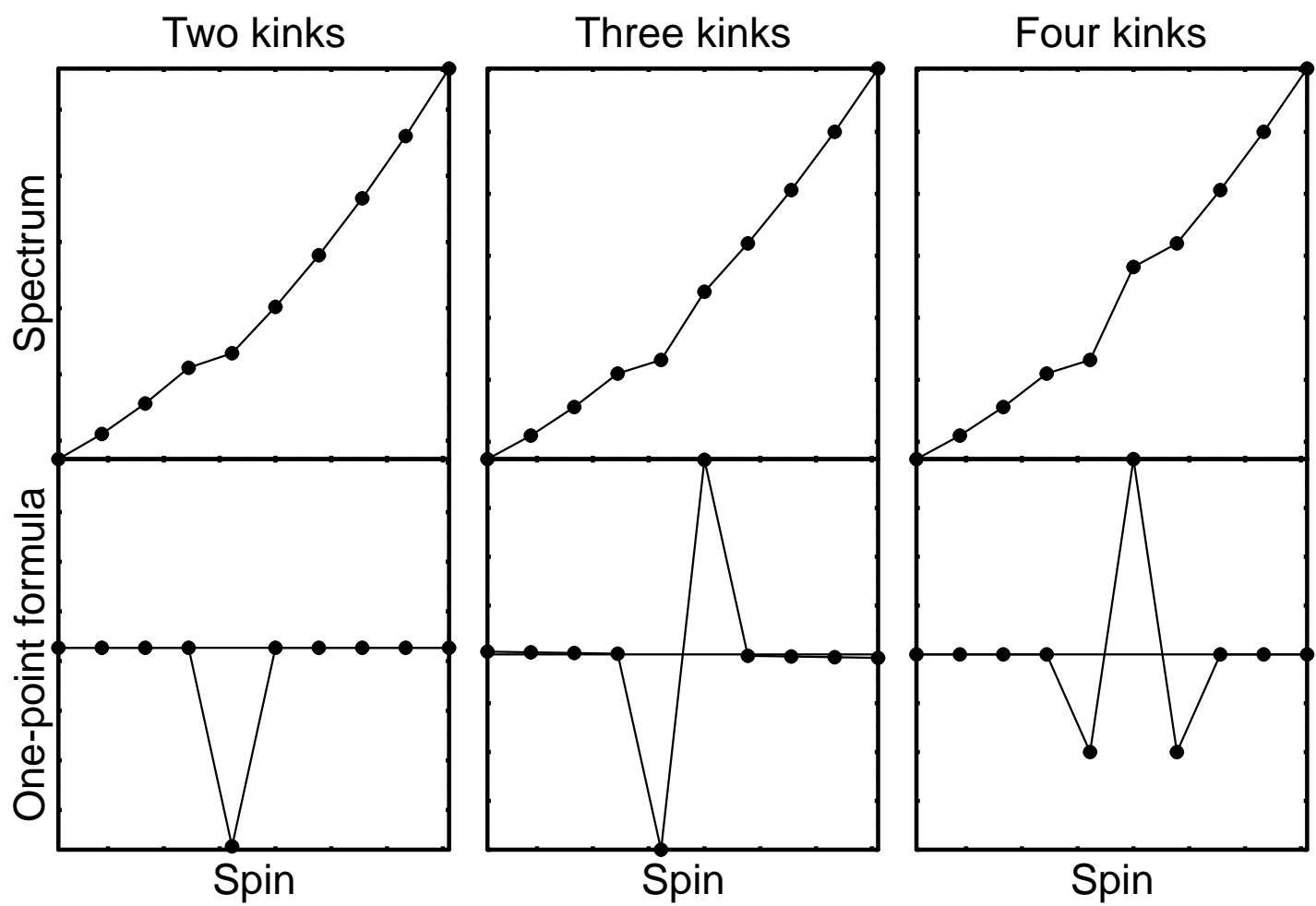


Fig. 3

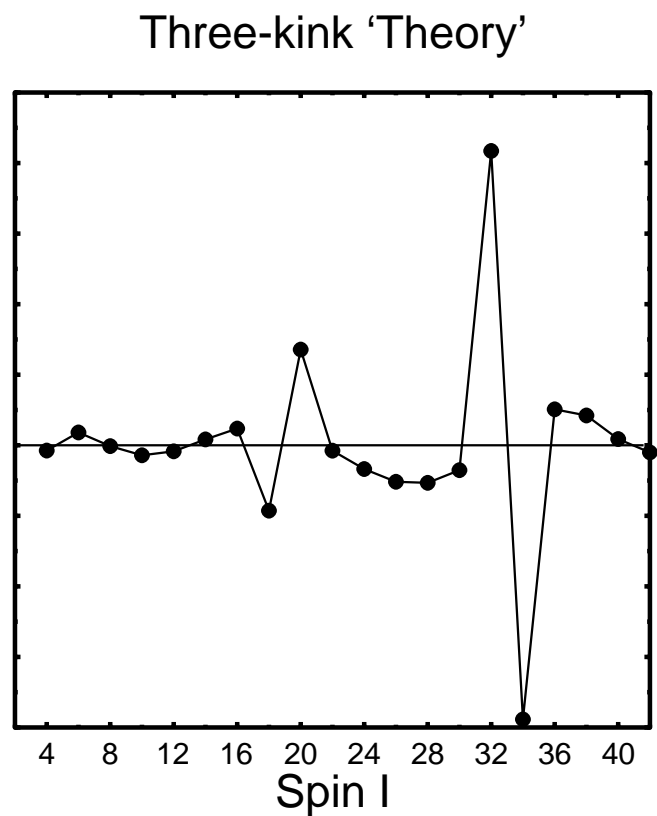
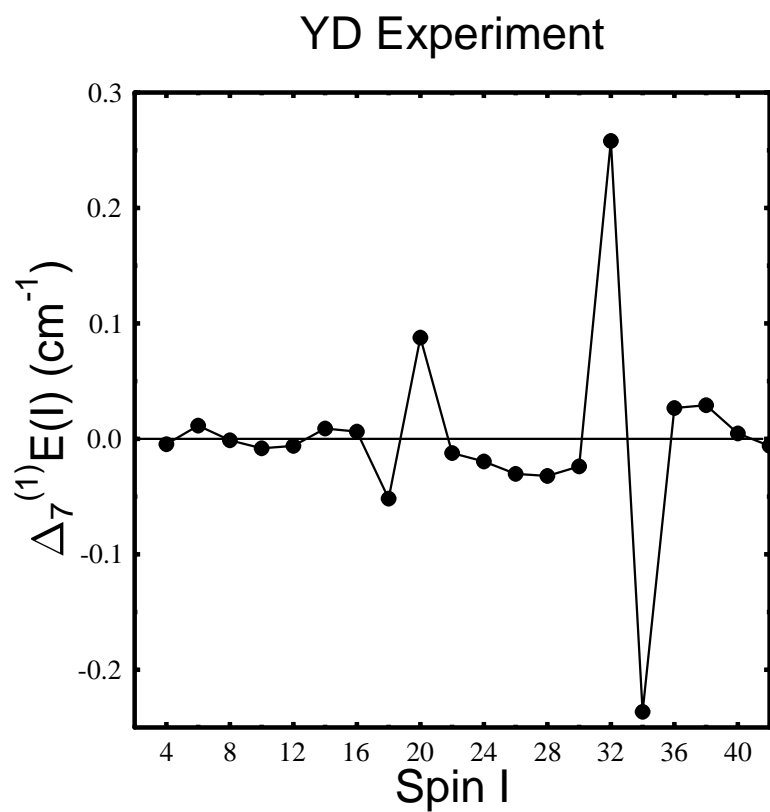


Fig. 4

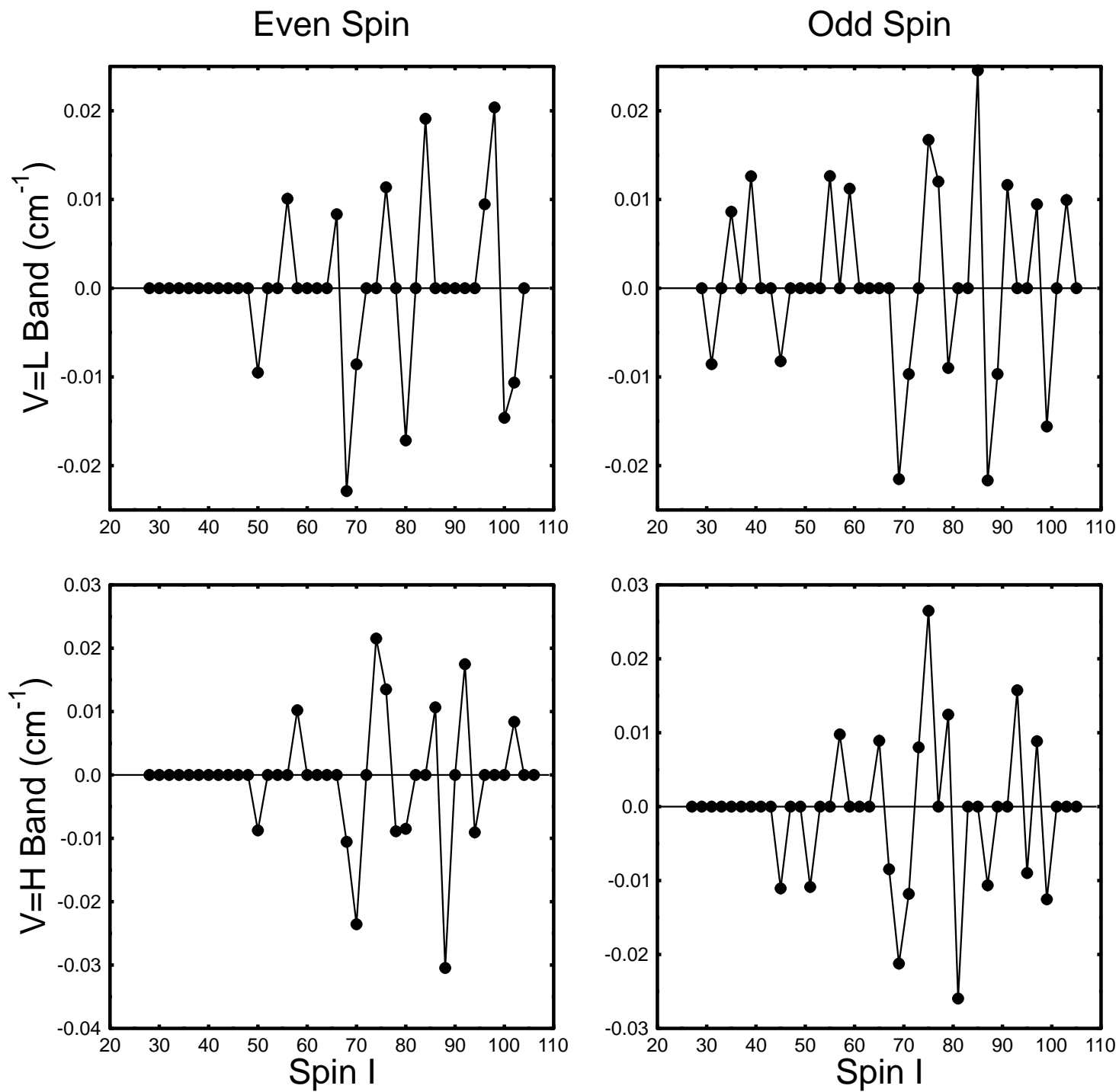


Fig. 5